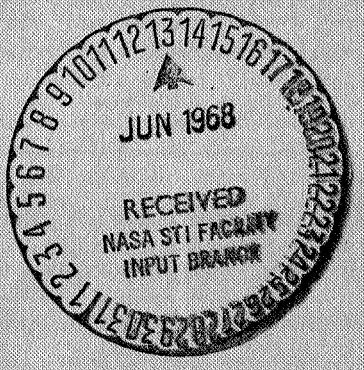
NASA CR-66618

IMPROVEMENT OF OXYGEN PARTIAL PRESSURE SENSOR

by William M. Hickam, Robert P. Goldstein,
and F. Reid Agnew



Prepared under Contract No. NAS 1-5924 by
WESTINGHOUSE ELECTRIC CORPORATION
Pittsburgh, Pennsylvania

for Langley Research Center

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

NASA CR-66618

IMPROVEMENT OF OXYGEN PARTIAL PRESSURE SENSOR

by William M. Hickam, Robert P. Goldstein,
and F. Reid Agnew

Prepared under Contract No. NAS 1-5924 by
WESTINGHOUSE ELECTRIC CORPORATION
Pittsburgh, Pennsylvania

for Langley Research Center

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

CONTENTS

Page

IMPROVEMENT OF OXYGEN PARTIAL PRESSURE SENSOR

by William M. Hickam, Robert P. Goldstein,
and F. Reid Agnew
Westinghouse Electric Corporation*

SUMMARY

A miniature flight type calcium stabilized zirconia solid electrolyte oxygen sensor originally developed by Westinghouse under NAS 1-4340 has been further studied toward making it applicable to oxygen monitoring of life support environment in capsule systems. Parameters associated with the electrical reliability of the sensor have been studied, feasibility of using a hermetically sealed gaseous oxygen reference has been investigated, and a miniature temperature controller designed and tested.

A major problem encountered in the present work, not encountered or anticipated based on the prior experience, was that of porosity of the walls of the double bore calcium stabilized zirconia tubes. The inability to obtain nonporous tubing of the established geometry continuously plagued the program. Material sufficient for making more than 50 sensors was obtained from the only known supplier in three different shipments. The manufacturer was consulted and made aware of the difficulty. In spite of a genuine effort on his part, satisfactory material was not obtainable. Every attempt was made to select sections from the large quantity of purchased double bore tubing with little success. The demonstrated oxygen monitoring features of the solid electrolyte sensor backed by the experience gained in Westinghouse over the past five years in marketing this instrument, support the many advantages of this type of oxygen sensor. This background warrants consideration of an alternate miniature sensor

*Westinghouse Research Laboratories, Pittsburgh, Pennsylvania 15235

geometry, or the use of machining techniques in achieving it in preference to the present extrusion method.

INTRODUCTION

In a previous program, NAS 1-4340, Westinghouse developed a prototype solid electrolyte flight type oxygen sensor and delivered units to NASA-Langley. The development program leading to this miniature oxygen sensor and its operating characteristics as known at that time were described in NASA Contractor Report CR-534 dated August, 1966. The electrolyte used was $(ZrO_2)_{.85}(CaO)_{.15}$. The sensor cell was in the form of a double bore tube in which the walls of each bore were coated with porous platinum films which served as electrodes. Platinum capillary tubes were attached to the sensor openings to provide entrance and exit ports for both the reference and sample gas. The cell was designed to operate at 850°C and required approximately 14 watts of DC power. The heater was wound on a ceramic form and made an integral part of the sensor by cementing the two assemblies together. The sensor and heater were packaged in a glass envelope containing potassium titanate for thermal insulation.

The sensor weighed 50 grams and occupied a volume of 18 cc. The output voltage signal, V, closely agreed to that defined by the Nernst equation:

$$V = \frac{RT}{nF} \ln \frac{P_1(O_2)}{P_2(O_2)} \qquad (1)$$

where R is the gas constant, T is the temperature in °K, n is taken as 4 from the reversible reaction $O_2 + 4e \rightleftharpoons 2\ O^{=}$, F is the Faraday constant, and $P_1(O_2)$ and $P_2(O_2)$ are the partial pressure of oxygen at the two electrodes. The prototype oxygen sensors of the original developmental program revealed properties that made it attractive as an oxygen sensor for life support systems. These included long shelf life, fast response time, precision of oxygen measurement

over the oxygen pressure range of interest, and insensitiveness to H_2O, CO_2, and N_2 commonly found in life support systems. These and other attractive features led to the conclusion of the desirability of further developing the sensor and other component parts required for a total prototype monitoring system.

Areas of further development and investigation undertaken under the present contract NAS 1-5924 include a study of various cell parameters as they might influence the electrical output signal, study of weight versus power trade-off, use of a hermetically sealed gaseous reference oxygen, and the delivery of four sensor systems with sensor, furnace, and miniature temperature controller.

WEIGHT VERSUS POWER TRADE-OFF

The oxygen sensors delivered under the earlier contract required 12-14 watts operating power. In view of the weight of only 50 grams per sensor (neglecting any auxiliary system components) and the power penalty of 0.5 lb. per watt additional improvements were desirable to reduce the power penalty. Two approaches were investigated: (1) reduction in heat losses by additional insulation and radiation shields; (2) operation of the system under reduced pressure.

Tests of additional insulation of potassium titanate at atmospheric pressure were carried out on a heater form fitted with a small ceramic two hole thermocouple tube. The thermocouple tube closely approximated the geometry of the sensor cell and provided a realistic mock-up of the oxygen sensor for power requirement studies.

The heater and thermocouple assembly equivalent to that of the oxygen sensor assembly was placed in a glass cylindrical container of approximately 6" diameter and surrounded by potassium titanate plus a covering of styrofoam. Power requirements were 10 watts at 850°C in air at atmospheric pressure. Compaction of the titanate suggested some further reduction in power requirements.

A second set-up was made in a glass bulb having a volume of 285 cc and a spherical geometry. The heater assembly was located in the center of the spherical shell and surrounded by well compacted titanate. The power consumption was 9.9 watts. A cooling curve for this cell is shown in Figure 1. On elimination of the power source at 850°C the sensor dropped to 770°C after 30 seconds. The earlier sensor assemblies had shown a drop to 720°C during the same time interval. This power requirement of approximately 10 watts achieved with the

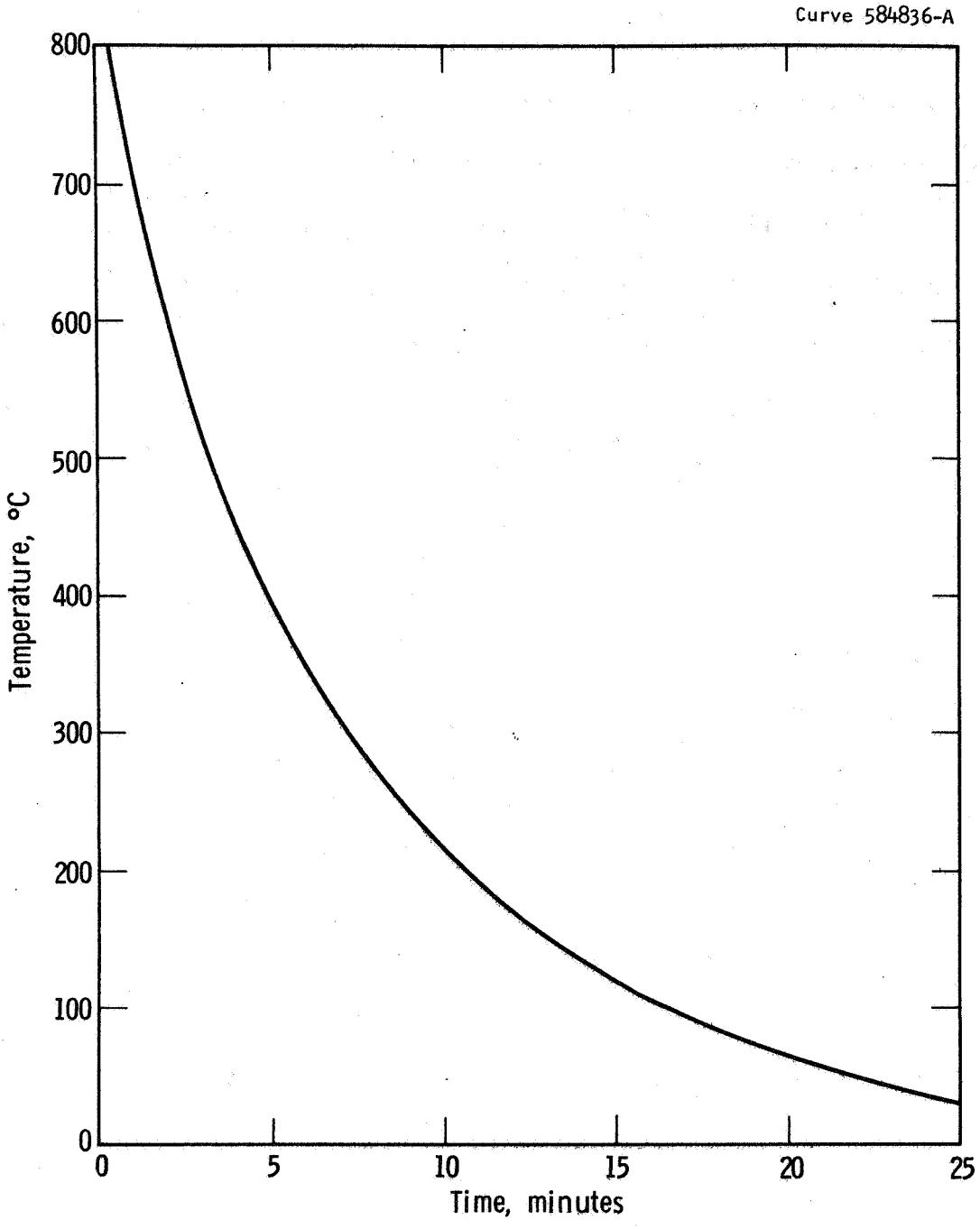


Fig. 1—Cooling curve (285cc 70gram cell) no power - no gas flow

large volume of insulation represents a reduction of 2-4 watts in the power requirements of the original units.

The influence of radiation shields was investigated. Metallic shields placed in the titanate were found to have little influence on the power requirements. This result plus the mechanical problems of supporting the shields led to the conclusion that this approach was not worthy of further consideration.

The heater containing the twin hole thermocouple tube was placed inside of a small bell jar and packed with potassium titanate. The bell jar was of the dimensions of the glass envelope used in making the original flight type sensors and equipped with a pump port for evacuation, a manometer, and a thermocouple gauge for measuring the air pressure in the bell jar. Power requirements for heating to 850°C were taken as a function of air pressure. At atmospheric pressure the power required to achieve 850°C was 12 watts and is in reasonable agreement with the earlier delivered sensors. Figure 2 is a plot of the air pressure versus power requirements to maintain 850°C. At 10^{-3} torr the power requirement was reduced to 4.7 watts, nearly a threefold reduction. The outgassing of the titanate prevented further improvement in vacuum.

In order to further explore the influence of lower pressure on sensor power requirements, a quantity of potassium was outgassed in a zirconia tube at 850°C under vacuum conditions for one hour. The gas evolution rate was then measured using the mass spectrometer. The composition of the evolved gas collected during a 15 minute interval at 850°C was as follows:

H_2	CO	CO_2	SO_2
6.92	24.48	67.68	0.92

The measured outgassing after baking for 1 hour at 850°C on a quantity of potassium titanate equal to that used in the previous flight type sensor was

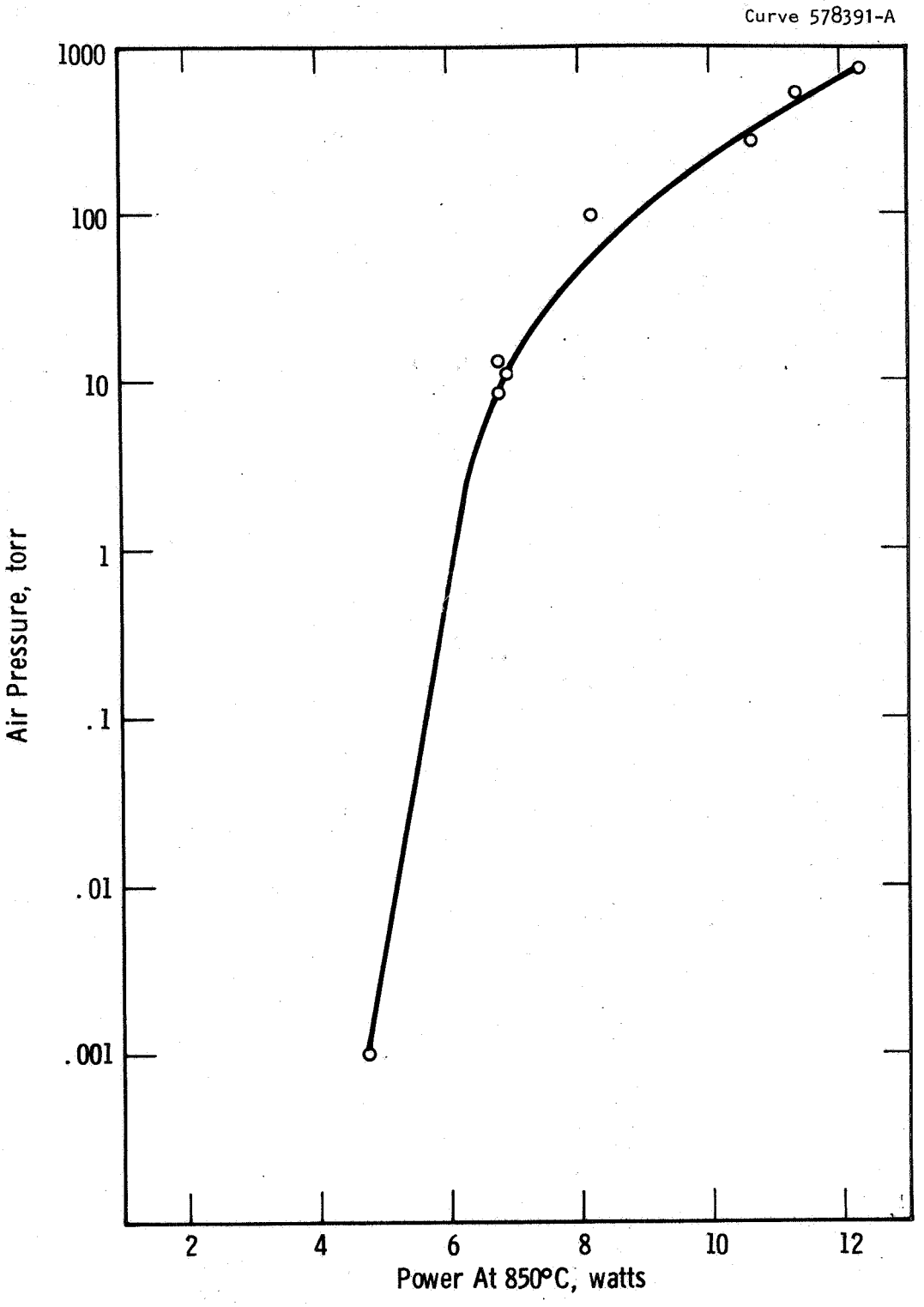


Fig. 2—Heater power at 850°C versus pressure using potassium titanate

4×10^{-6} cc-atm/sec. The potassium titanate changed from a white to a light purple color during the bake. A continuation of the measured outgassing rate during a 100-day mission would result in the evolution of 34.4 cc-atm of gas. However, only a small fraction of the total titanate used for insulation would be subjected to this high temperature and therefore the total outgassing from a sensor in operation for this total time period might be expected to be several orders of magnitude smaller. When the outgassed titanate was tested in heater set-up equivalent to the sensor, the power requirement to achieve 850°C operating temperature under vacuum was 3.76 watts as compared to 4.76 watts in the set-up using the undegassed titanate. This provides evidence that the high temperature degassing did not degrade the thermal insulation properties of the titanate but rather resulted in sizable reduction in power requirements in a design equivalent to the originally supplied sensors.

REFERENCE SUPPLY

The solid electrolyte oxygen sensor yields an output voltage which is interpretable by comparison to a known oxygen pressure. Many means for achieving a known oxygen pressure are known. The storage in a hermetically sealed system of a fixed quantity of gas similar in composition and pressure to that being sampled offers many advantages. The system would restrict the exposure of cell to foreign materials which might result in decreased life. The voltage output of the cell at operational times would be low and no chemical alteration of the electrolyte composition would be expected. The reference system might operate at cabin temperature and would not require elaborate temperature control or appreciable additional power. Metal-metal oxide mixtures are frequently used as a source of oxygen but in this system they would have to be thoroughly investigated in order to establish their usefulness as a reference on a 100-day mission. Furthermore, in order to achieve a desirable oxygen reference, temperature control of the encapsulated metal-metal oxide would be more complicated than using a gaseous reference where corrections based upon a temperature measurement without control is simple.

In the use of a gaseous reference such as air at atmospheric pressure, a major concern is that the system remains hermetically sealed and that controllable impurities associated with the system do not deplete the oxygen. A study was made of the use of a sealed reference using a closed end solid electrolyte cell of much larger dimensions than that of the flight sensor. A closed end tube of the composition used in the miniature sensor $(ZrO_2)_{.85}(CaO)_{.15}$ was employed. The cell had a length of 8 inches and an outside diameter of approximately 3/16 inch with a 1/32 inch wall thickness. Porous platinum electrodes were located on the inner and outer surfaces to serve as electrodes.

The open end of the cell was attached to the reference oxygen system by means of a rubber O-ring seal. The reference oxygen was stored in a 75 cc stainless steel container equipped with metal valves. Attachment of a manometer and valve for evacuation completed the set-up shown in Figure 3.

The response of the cell to oxygen pressure changes in the reference volume is shown in Figure 4. The reference used is air at atmospheric pressure. Under this no flow condition of referenced gas sample, the cell output voltage closely approximates the theoretically predicted output. In Figure 5 is shown the results of a seven day test using a hermetically sealed oxygen reference in the 75 cc container. The total scatter in the recorded data is 0.4 mv which is equivalent to a pressure change of approximately 12 torr. Figure 5 also shows the recorded variations in atmospheric pressure during this period. The close agreement of the shape of the curves suggests that the measured voltage changes are associated with changes in the atmospheric pressure used as a reference. The sealed reference volume was at a pressure of 782.6 torr.

In the use of a sealed oxygen reference volume, changes in the absolute temperature of the reference gas will be proportional to the oxygen pressure. Figure 6 is a photograph of the experimental set-up used for obtaining cell response versus temperature of the sealed reference gas. Shown is the standard Westinghouse closed end cell, temperature controller, and a sealed glass 500 cc volume with heater wound on it. The temperature was measured with a thermocouple located in a thermocouple wall within the glass volume. The 500 cc volume of which the temperature was changed represents approximately 95% of the total sealed volume. Figure 7 is a semi-log plot of the absolute temperature versus cell output. The points approximate a straight line as expected and the voltage output is in reasonable agreement with that expected from the relationship

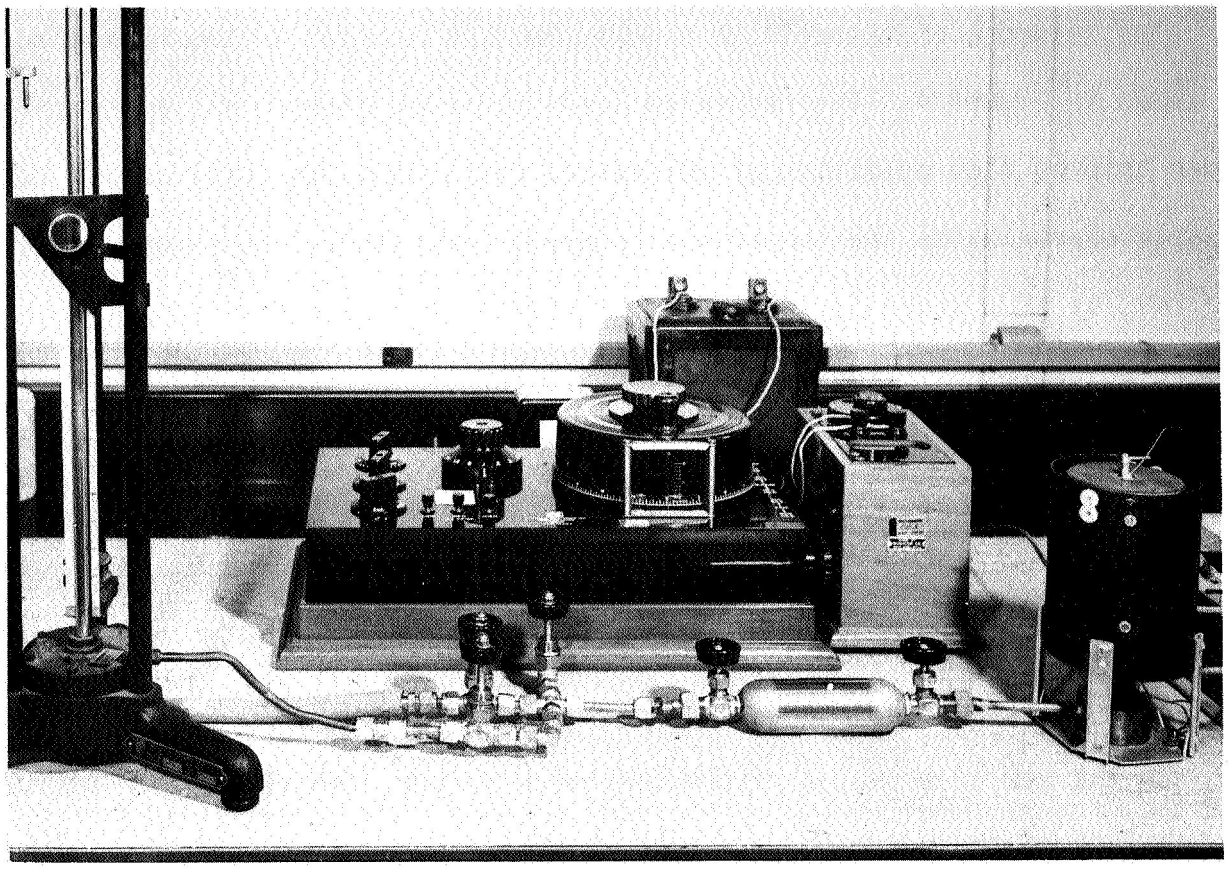


Fig. 3—Reference supply test setup

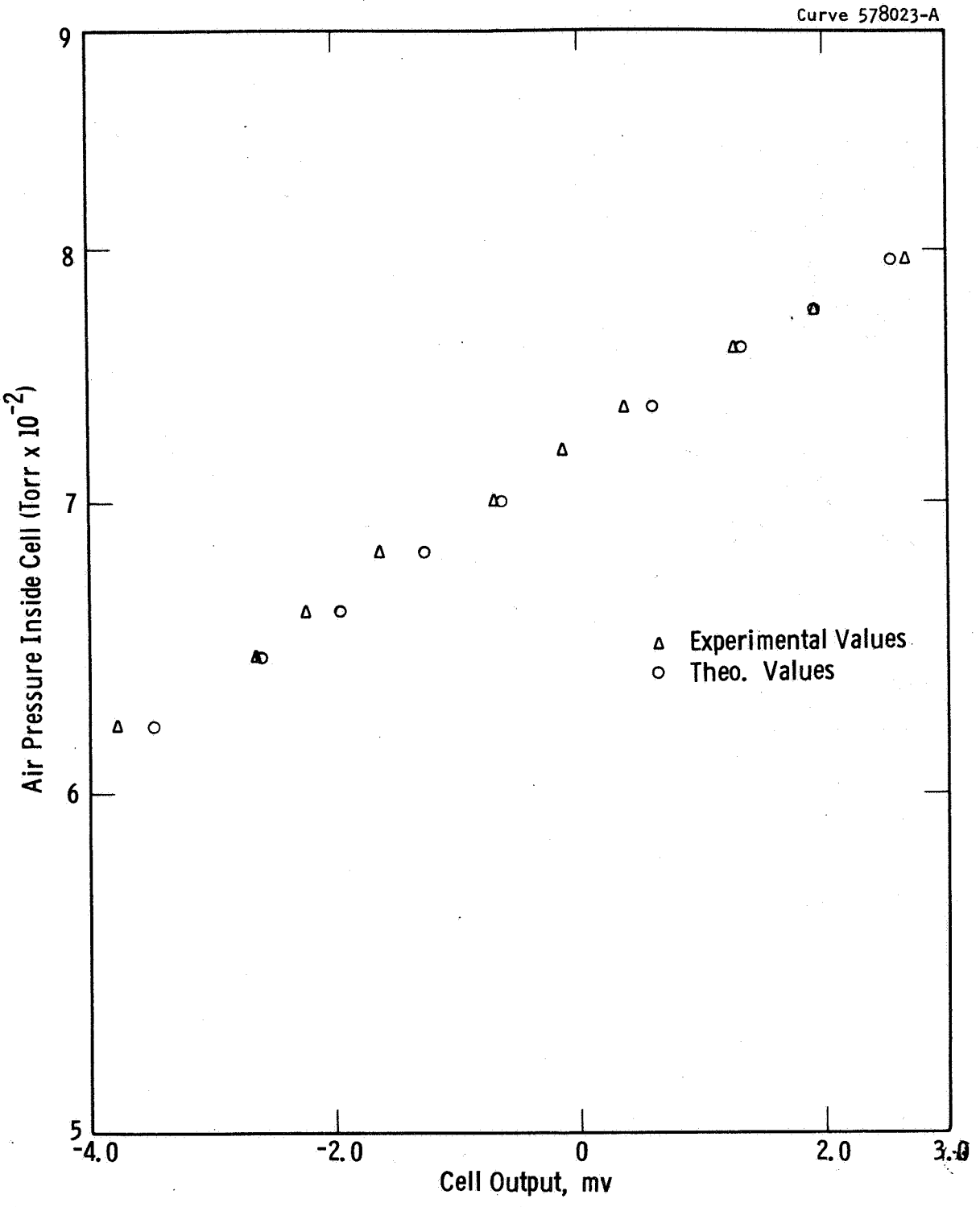


Fig. 4 —Cell output as a function of air pressure in sealed reference volume

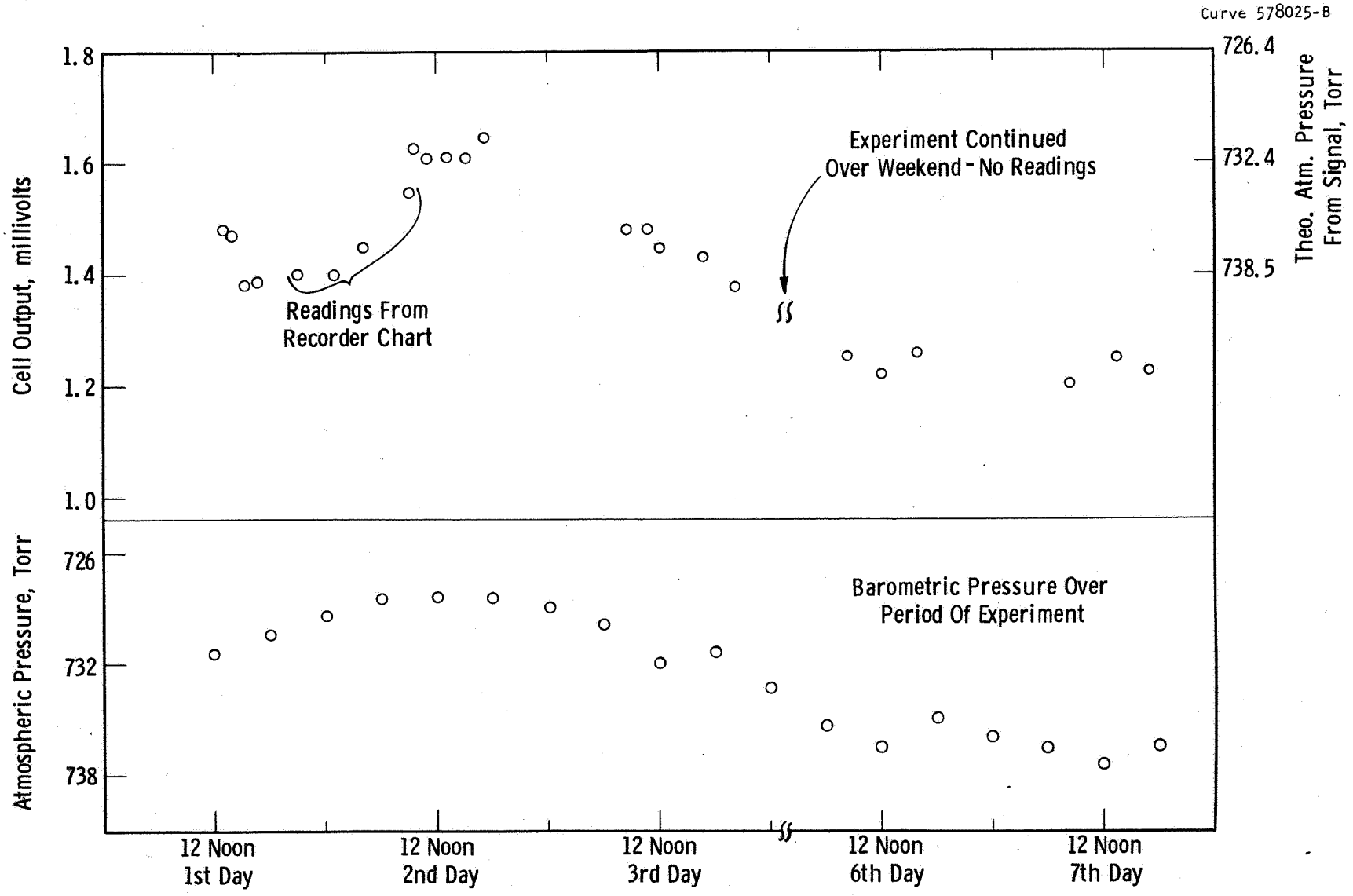


Fig. 5 —Cell output as a function of time with sealed reference (Air - 782.5 Torr)

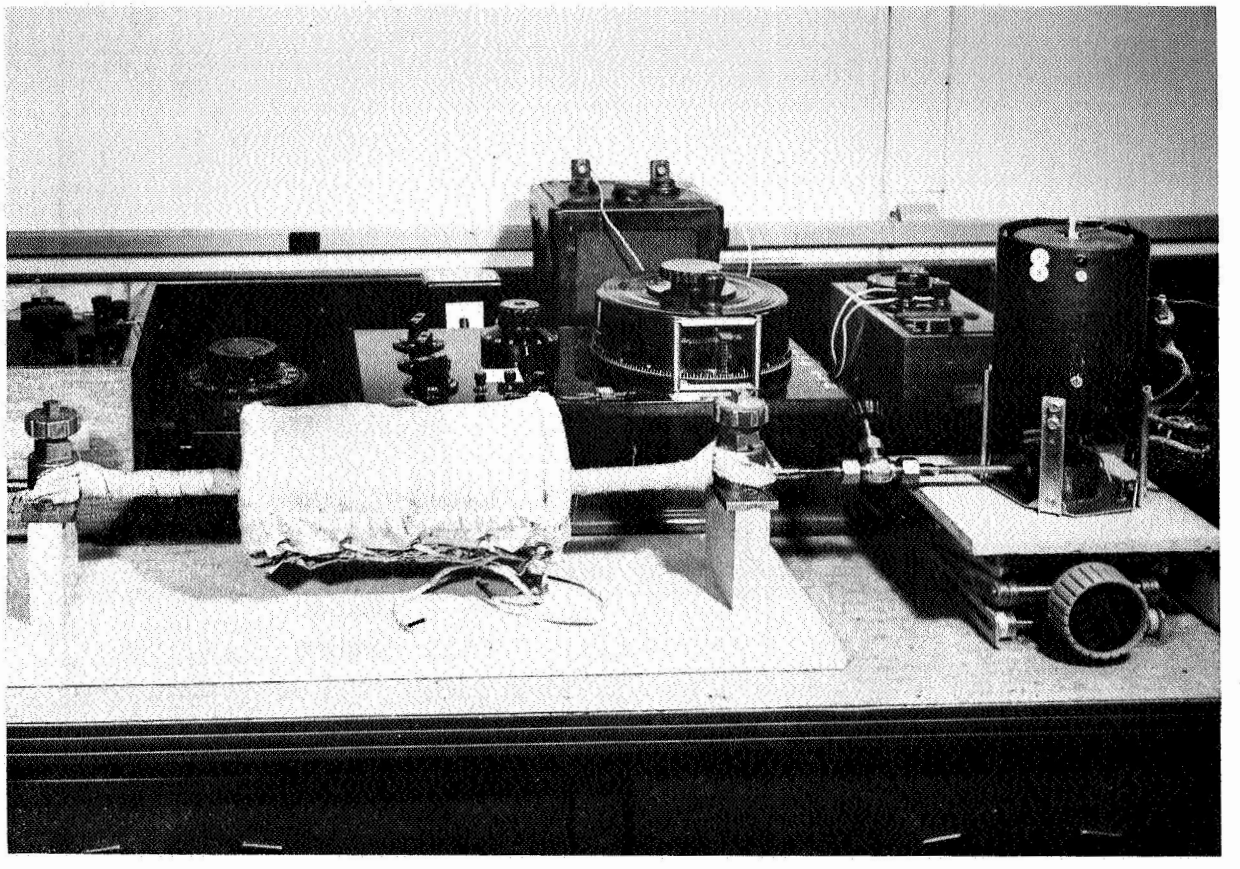


Fig. 6—Reference supply with heater

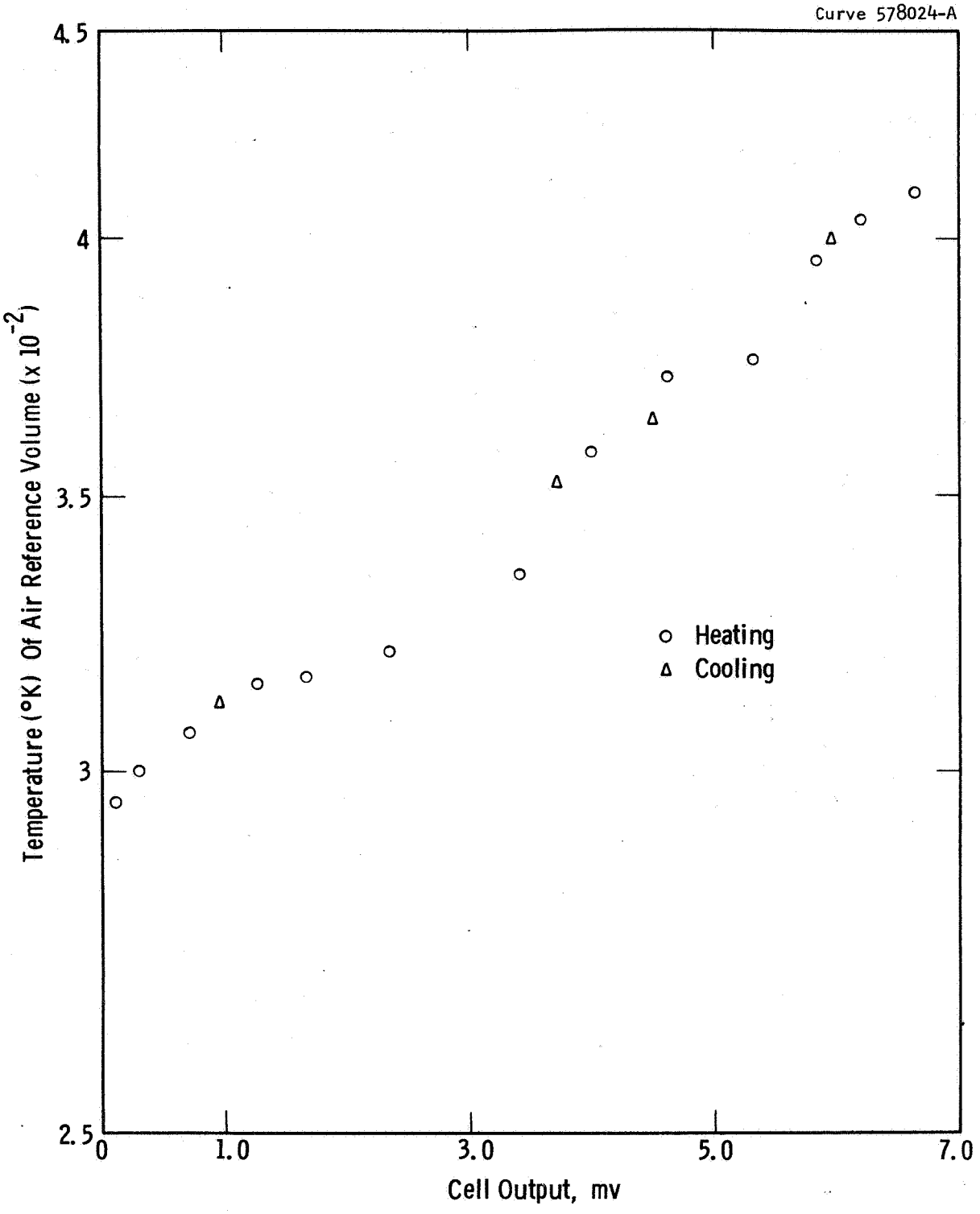


Fig. 7 —Cell output as a function of sealed air volume temperature

of absolute temperature to pressure. In the use of a hermetically sealed reference gas it may be desirable to monitor the temperature changes and correct the cell output reading rather than undergo the complications of maintaining the reference at constant temperature.

SENSOR FABRICATION

Figure 8 shows the parts that are used in the fabrication of the sensor. Figure 9 shows the sensor as prepared for encapsulation. The connections for the heater winding, thermocouple, platinum resistance thermometer, and cell output are visible on the tube press at the left side. The sensor cell can be seen in the center with the fired glass seals to the platinum tubing on each end. The two cross-over wires connecting the platinum tubes to increase continuity reliability are shown to the right near the platinum to tubing connection. The tubing is beaded in preparation for sealing to the glass envelope.

The program has been plagued as a result of two difficulties encountered: (1) porosity of the line stabilized zirconium sensor material; (2) hermetically sealing of platinum capillary entrance and exit tubing the coil. In regards to the first problem, it is believed that some undefined change has occurred in the fabrication of the material as received from the only known supplier which results in porosity of the material to an extent not encountered under the prior contract. Extreme efforts have been made in cooperation with the supplier in order to understand and eliminate this problem without a high degree of success. Although the problem was not uncovered until the final assembly of the sensor constructed for test and delivery early in the program, it is concluded that the porosity is associated with the material as received rather than the result of any processing during fabrication. Unprocessed tubes received at a later date revealed a high degree of porosity under helium leak test. In regard to the sealing problem, this was at times confused with the porosity problem, but it can be individually considered as a portion of the assembly needing further attention. Since the porosity problem was unanticipated, the separation of the

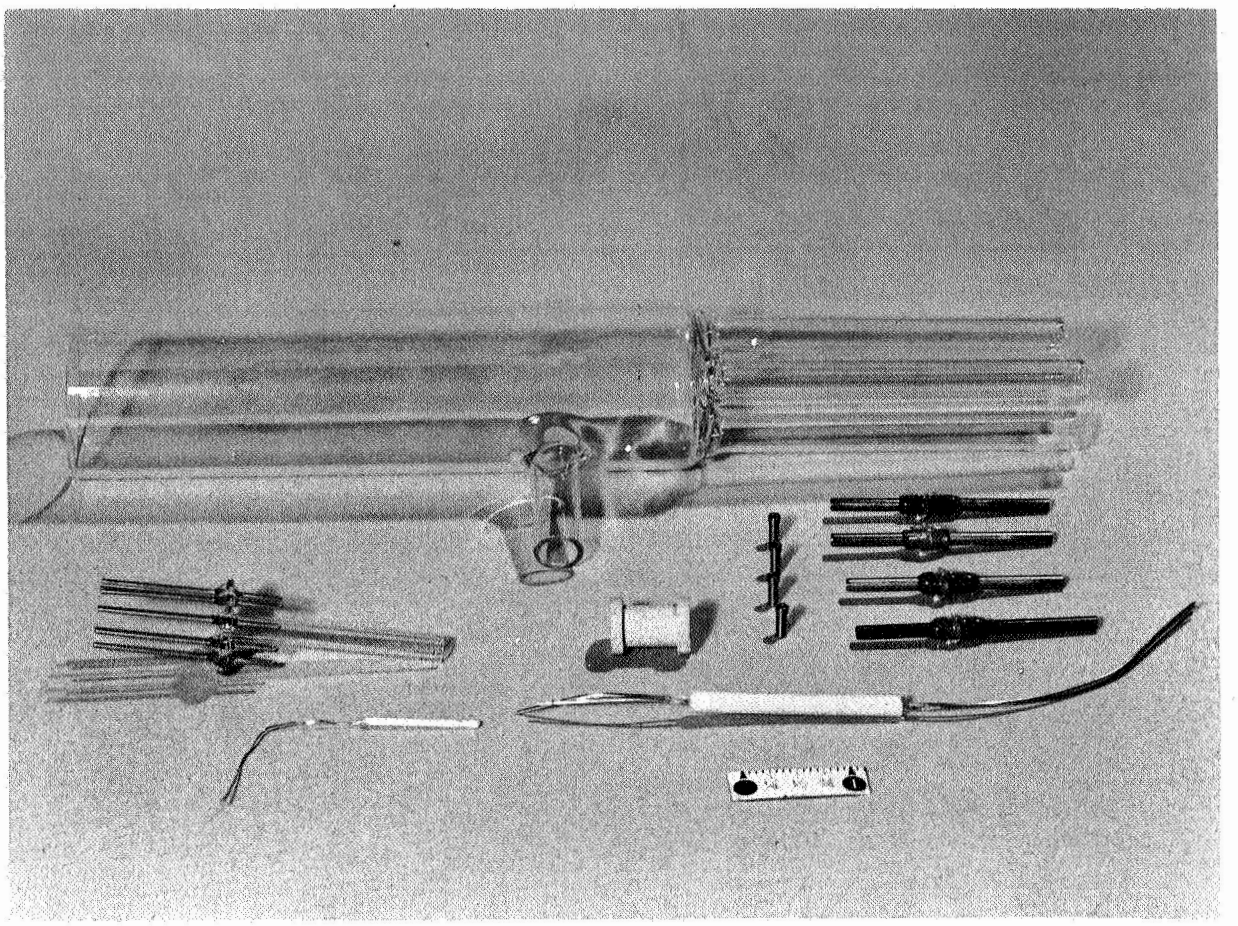


Fig. 8—Oxygen sensor components

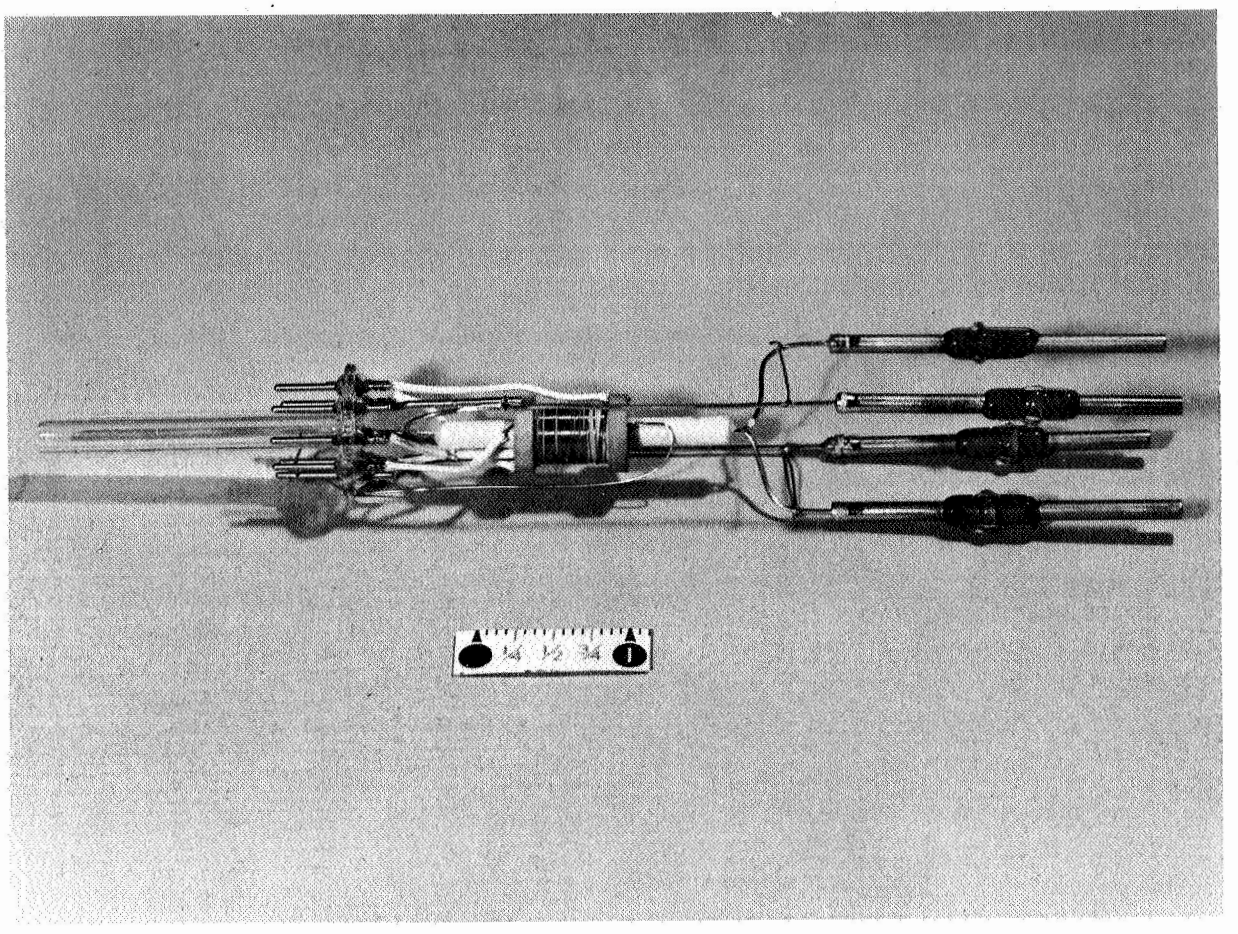


Fig. 9—Sensor sub-assembly

two problems at a stage of partial assembly of the miniature sensors was even more perplexing.

Opening of the sintered glass seal joining the platinum to the solid electrolyte as a result of temperature cycling was encountered. In order to reduce the severity of temperature cycling a longer sensor cell of 2 inches compared to the original 1 inch was employed in the program. The final sensors delivered were of 2 inch length. Primarily as a result of this extension in length, the power requirements for operation at 850°C in air at atmospheric pressure increased to about 25 watts as compared with the original units of 12-14 watts. Only by evacuation of these cells insulated with potassium titanate was it possible to reduce the power requirements to approximately 10 watts. This power consumption is one and one-half times that found for the sensors of the original design under evacuated conditions. A return to the earlier design and even further miniaturization is clearly indicated in order to achieve cells of minimum power requirements.

To prepare 4 flight type oxygen sensor cells has required a careful re-evaluation of fabrication techniques and constructional materials. It was first necessary to develop a suitable method for sealing platinum tubing to the zirconia cells. The most successful material was found to be Pyroceram (No. 0080-5M28514, Corning Glass Company). Pyroceram powder (200 mesh) is first mixed with cellulose acetate cement and applied to the junction between platinum and zirconia. The joint is then slowly heated to 800°C; the cement decomposes and the Pyroceram fuses into a glassy, gas-tight joint having great strength. To prevent operating heat from destroying the seal, the zirconia cell was lengthened from 1 to 2 inches. The estimated seal temperature does not exceed 700°C.

It was then found that the fabricating procedures employed in the manufacture of the zirconia tubes were not uniform and the units delivered (after a waiting period of 16 weeks) were extremely porous. Investigation showed that porosity can be remedied by "soaking" of the zirconia tubes in an inert atmosphere at 1800°C. This was done with the available tubes, and six units have been constructed.

The packaging of the sensor in the glass envelope and the attachment of the electrical and gas ports during final assembly is felt to be of good mechanical design. The completed sensor is shown in Figure 10. The draw tube at the left has been sealed after the sensor has been evacuated.

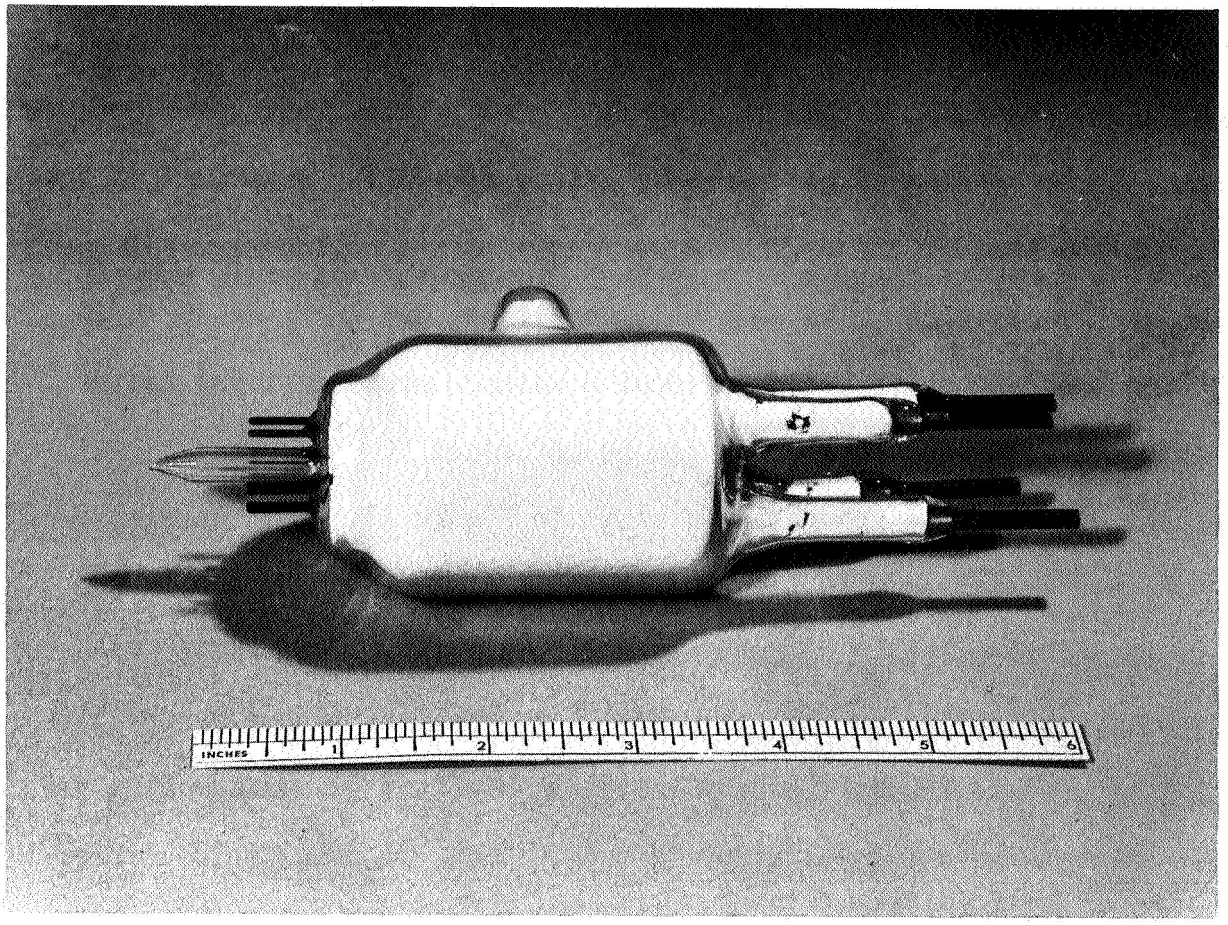


Fig. 10—Oxygen sensor

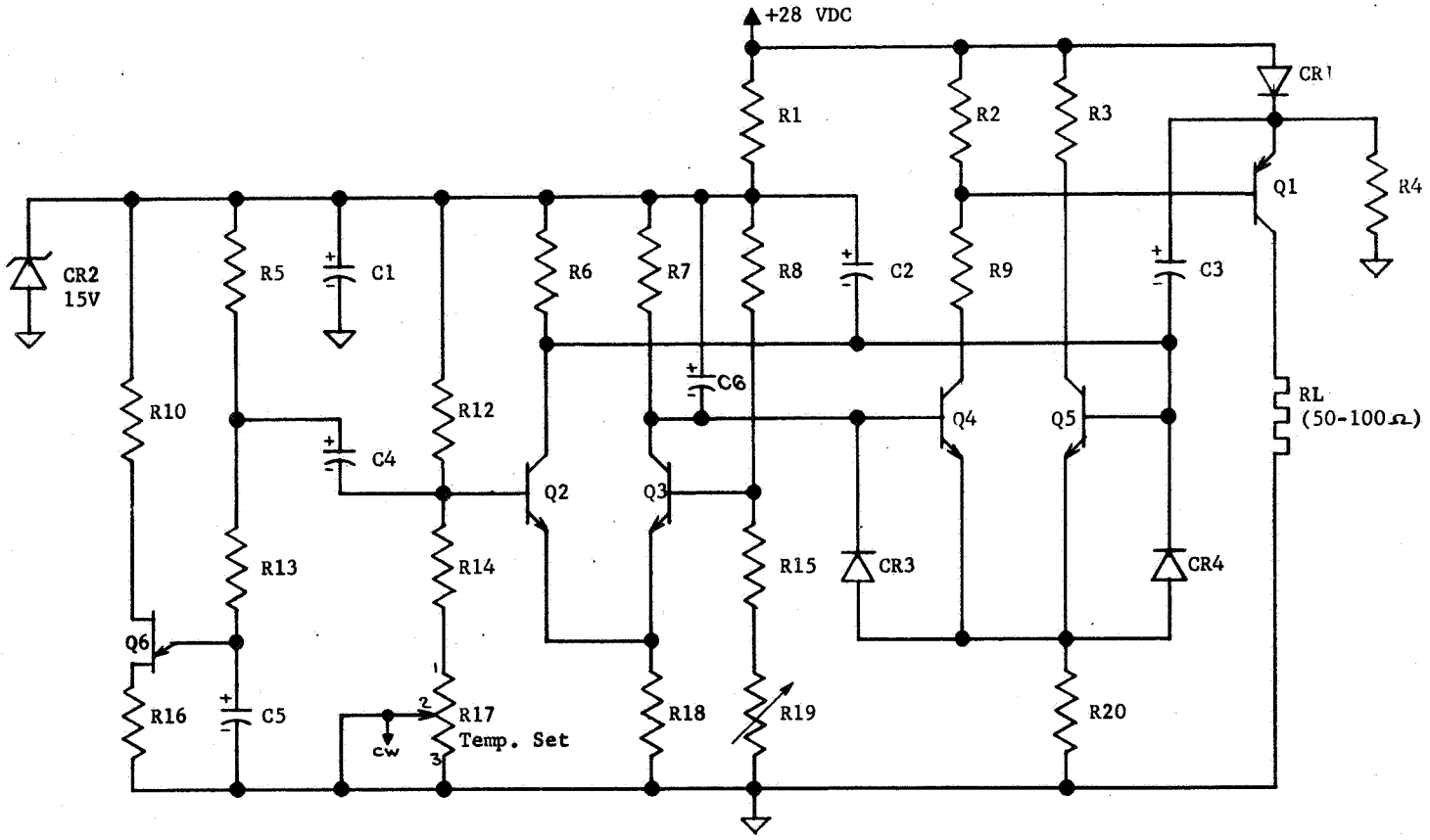
TEMPERATURE CONTROLLER

Commensurate with power and weight reduction a temperature controller with maximum efficiency has been designed, built, and tested. To achieve maximum efficiency the temperature controller was designed to maintain cell temperature by pulse width modulation (proportional on-off) rather than class A control of heater voltage. The power output section of the controller thus approaches 100% efficiency. The preceding signal sections of the controller draw a fixed power which depends somewhat on the maximum power requirements of the heater for which the controller is designed. The controller built was designed for up to 20 watts and the constant power drain is about 2 watts. When the final heater requirements are known the controller can be optimized.

The controller, whose schematic is shown in Figure 11, is in essence a differential d-c amplifier with the addition of a sawtooth reference which drives the output from cutoff to saturation at about 1 kc. The ratio of on to off is directly controlled by the ratio of the temperature sensor error voltage to the sawtooth reference peak-to-peak voltage. When set to maximum gain the controller sawtooth reference is about 25 mvpp. Thus, 25 mvpp, which corresponds to about 30°C, variation of temperature sensor signal will drive the output from full on to full off.

For best stability the heater should be designed for twice the power required to maintain 850°C. The controller output at operating temperature will then be a 1 kc square wave with about 50% on time. At warm-up the heater will receive full 25 vdc. Above the proportional temperature band the controller output is zero.

The linearity of the proportional zone is determined primarily by the linearity of the sawtooth reference. Less than perfect filtering by C1 is used



R1, R2, R3, R9 - 470Ω
R4 - 4.7K
R5 - 22Ω
R6, R7, R14 - 2000Ω
R8, R12 - 3830Ω
R10, R18 - 1K
R13 - 12K
R16 - 47Ω
R15 - 1820Ω

R17 - 500Ω
R19 - 400 @850°C, Plat. Temp. Sens.
R20 - 330Ω
CR1 - 1N2069
CR2 - 1N965B
CR3, CR4 - 1N914
Q1 - 2N1038
Q2, Q3 - 12A8
Q4, Q5 - 2N1711

Q6 - 2N2646
C1, C4 - 3.3μf 15V
C2, C6 - .033μf 35V
C3, C5 - .1μf 35V

NASA TEMPERATURE CONTROLLER

Fig. 11—Circuit schematic of temperature controller

to eliminate a discontinuous gain curve near maximum power. Positive feedback by C3 is used to approximate true bistable output.

The controller was evaluated with a sensor assembly which required 7.25 watts at 850°C. No visible temperature overshoot was observed and the cell output voltage showed no detectable variation with time.

The circuit was first breadboarded as shown in Figure 12, and tested. Then a printed circuit model of the temperature controller, per Figures 13 and 14 (#2127B31) was built. A card edge connector was selected on the basis of short lead time. The printed circuit portion of the connector is gold-plated to assure good long-term contact. Five complete controllers were assembled. No adverse effects to the measurement circuit were noted due to the ripple and polarity of the heater power supply, the electrical leakage from the heater windings, or the stray magnetic field.

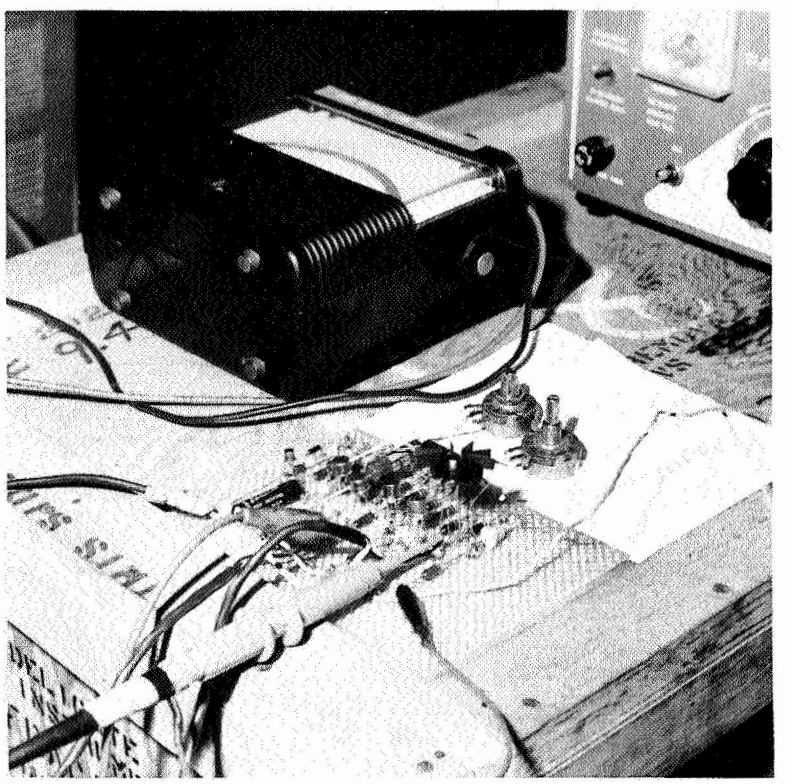


Fig. 12—Breadboard model of temperature controller

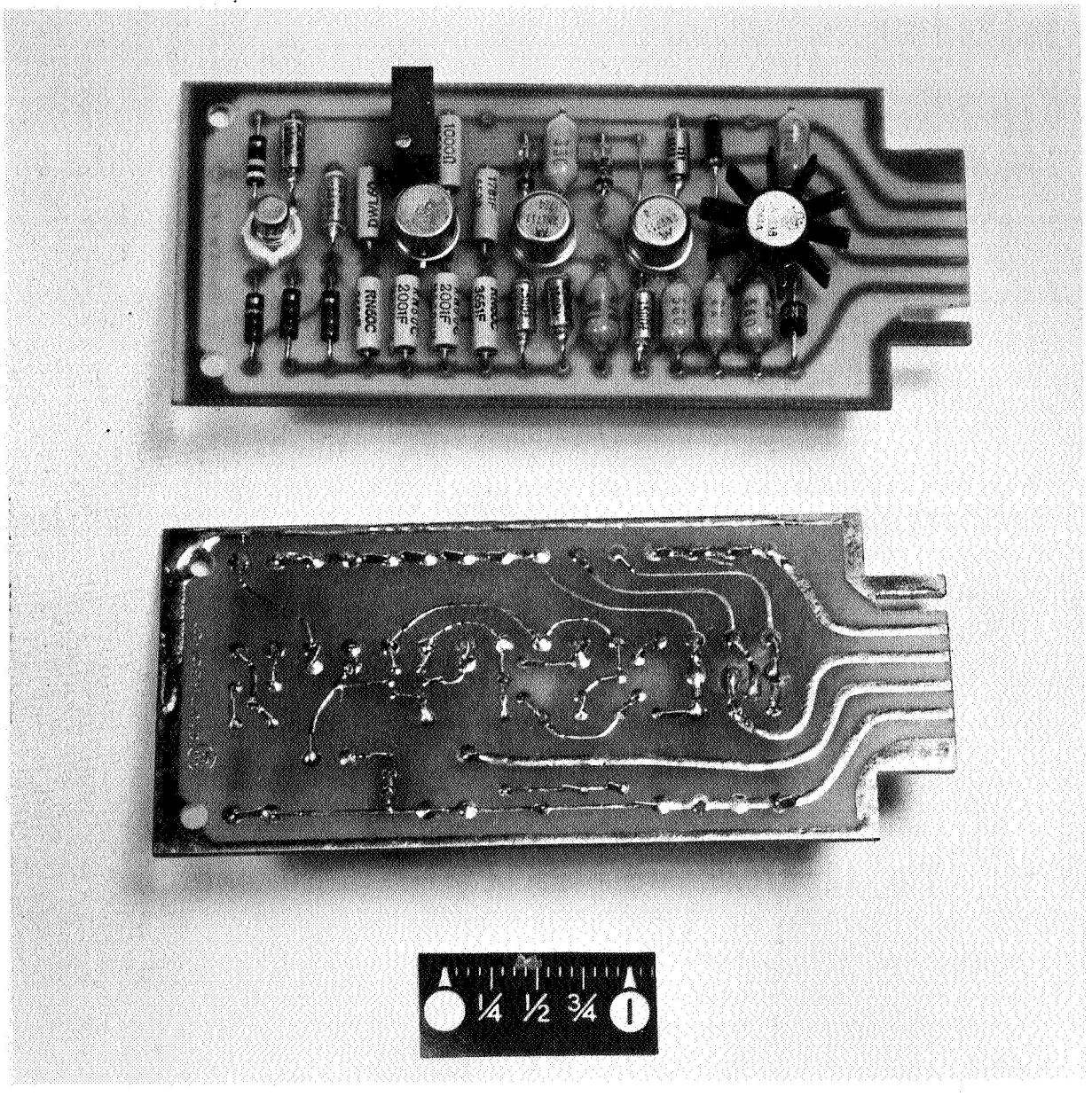
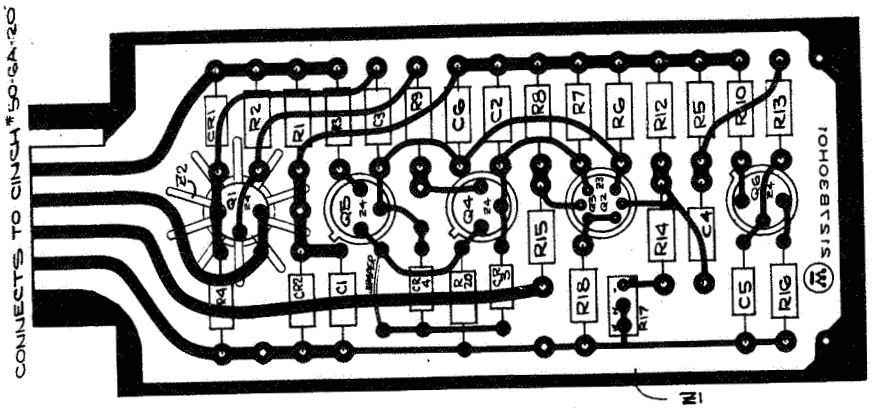


Fig. 13—Printed circuit board of temperature controller



SCALE: 2=1

SYMBOL	DESCRIPTION
R1	470Ω 2W WIREWOUND 5% AXICHM
R2	470Ω 2W WIREWOUND 5% AXIOHM
R3	470Ω 2W WIREWOUND 5% AXIOHM
R4	4.7K 2W WIREWOUND 5% AXICHM
R5	22Ω ¼W 5% LITTLE DEVIL
R6	2000Ω ⅛W METAL FILM ½% "N-80-TO
R7	2000Ω ⅛W METAL FILM ½% "N-80-TO
R8	3830Ω ⅛W METAL FILM ½% "N-80-TO
R9	470Ω 2W WIREWOUND 5% AXICHM
R10	1K ¼W 5% LITTLE DEVIL
R12	3830Ω ⅛W METAL FILM 1% "N-80-TO
R13	12K ¼W 5%
R14	2000Ω ⅛W METAL FILM 1% "N-80-TO
R15	1820Ω ⅛W METAL FILM 1% "N-80-TO
R16	47Ω ¼W 5% LITTLE DEVIL
R17	500Ω TRIMPOT, BOURNS P/N 3250W-1-501 W.W. REWOUND
R18	1K ⅛W METAL FILM 1% "NL80-TO
R20	330Ω 2W WIREWOUND 5% AXICHM
CR1	IN2069 750ma 200V DIODE T.I.
CR2	IN5258 15V±5% 400mW ZENER I.R.
CR3	IN914
CR4	IN914
Q1	2N1038 TRANSISTOR (TO-5 STYLE) T.I.
Q2-Q3	12AB DUAL NPN TRANSISTOR G.E.
Q4	2N1711
Q5	2N1711
Q6	2N2646 UNIJUNCTION G.E.
C1	3.3μf 15WVDC SOLID TANTALUM T.I.#335FP015A2
C2	.033μf 35WVDC SOLID TANTALUM T.I.#333FP035A2
C3	.1μf 35WVDC SOLID TANTALUM T.I.#104FP035A2
C4	3.3μf 15WVDC SOLID TANTALUM T.I.#335FP015A2
C5	.1μf 35 WVDC SOLID TANTALUM T.I.#104FP035A2
C6	.033μf 35 WVDC SOLID TANTALUM T.I.#333FP035A2
Z1	PRINTED BOARD W.#2127B30H01
Z2	HEAT SINK WAKEFIELD #NF205
Z3	MOUNTING PAD THERMALLOY #7717-60
Z4	MOUNTING PAD THERMALLOY #7717-44 (4 REQD)

ITEM	USED WITH	REF. DWG. See Dwg. 1234A36 FOR Cutting & Drilling
MODEL		

WESTINGHOUSE ELECTRIC CORPORATION

TITLE NASA TEMPERATURE CONTROLLER PARTS PLACEMENT

TOLERANCES			DIMENSIONS NOT TO SCALE
TWO PLACE DEC. ±.020 THREE PLACE DEC. ±.005 ANGLE ±1/2° UNLESS OTHERWISE NOTED	DFTM. N Phillips 12-21-64		REV.
	CHKD. JV Call 2-9-65	2127B31	
	APPD. [signature] 2-9-65		
	APPD.		

SCIENTIFIC EQUIPMENT DEPT. – E.C. & S.P. PGH., PA. 15221

Fig. 14—Parts layout of temperature controller

CONCLUSIONS

It was necessary to modify the sensor design from the one that was originally intended to be used because of failures in the zirconia to platinum glass seals. The failures occurred partly in fabrication and partly as a result of temperature cycling. In order to overcome the difficulty, the sensor length was increased from one to two inches. This removed the seal further from the high temperature region. A drawing showing this change and the design of the sensors delivered under this contract is presented in Figure 15. The increased length resulted in an increase in the power required as mentioned earlier. Figure 16 is a photograph of both the final sensor and its temperature controller.

The functioning of the temperature controller with a final sensor is shown in Figure 17. The sensor unit was evacuated and had a power consumption in the order of 10 watts. The sensor required fifteen minutes to reach operating temperature and shows that constant temperature is satisfactorily maintained. The cooling curve from 850°C was based on the cutoff of power at time zero.

The functioning of the completed sensor is illustrated in Figure 18. Duplicate data at flow rates of 0.080 and 0.060 SCFH are shown covering an oxygen concentration of 6-40% oxygen in nitrogen. A reasonable comparison is obtained with the theoretical curve for 850°C operation. Because of the difficulties encountered in obtaining the ZrO_2 . CaO electrolyte geometry from the only known supplier in a leak-proof form and because of sealing difficulties, a total of 4 units were delivered. In order to achieve these results, a total of 15 to 20 units were processed to varying degrees of completion and scrapped due to failures encountered.

Temperature regulators for the sensor were designed and 10 were built. The units were found satisfactory for regulating the oxygen flight sensor. A total of four units were fabricated and delivered to NASA as a part of the contract.

It is the conclusion of the contract that the principle of the oxygen sensor is sound. Additional work in the electrolyte fabrication and sealing is needed to yield units with greater reliability. A new sealing material for joining the ZrO_2 . CaO to metal has recently been found and shows great promise of solving the sealing problem.

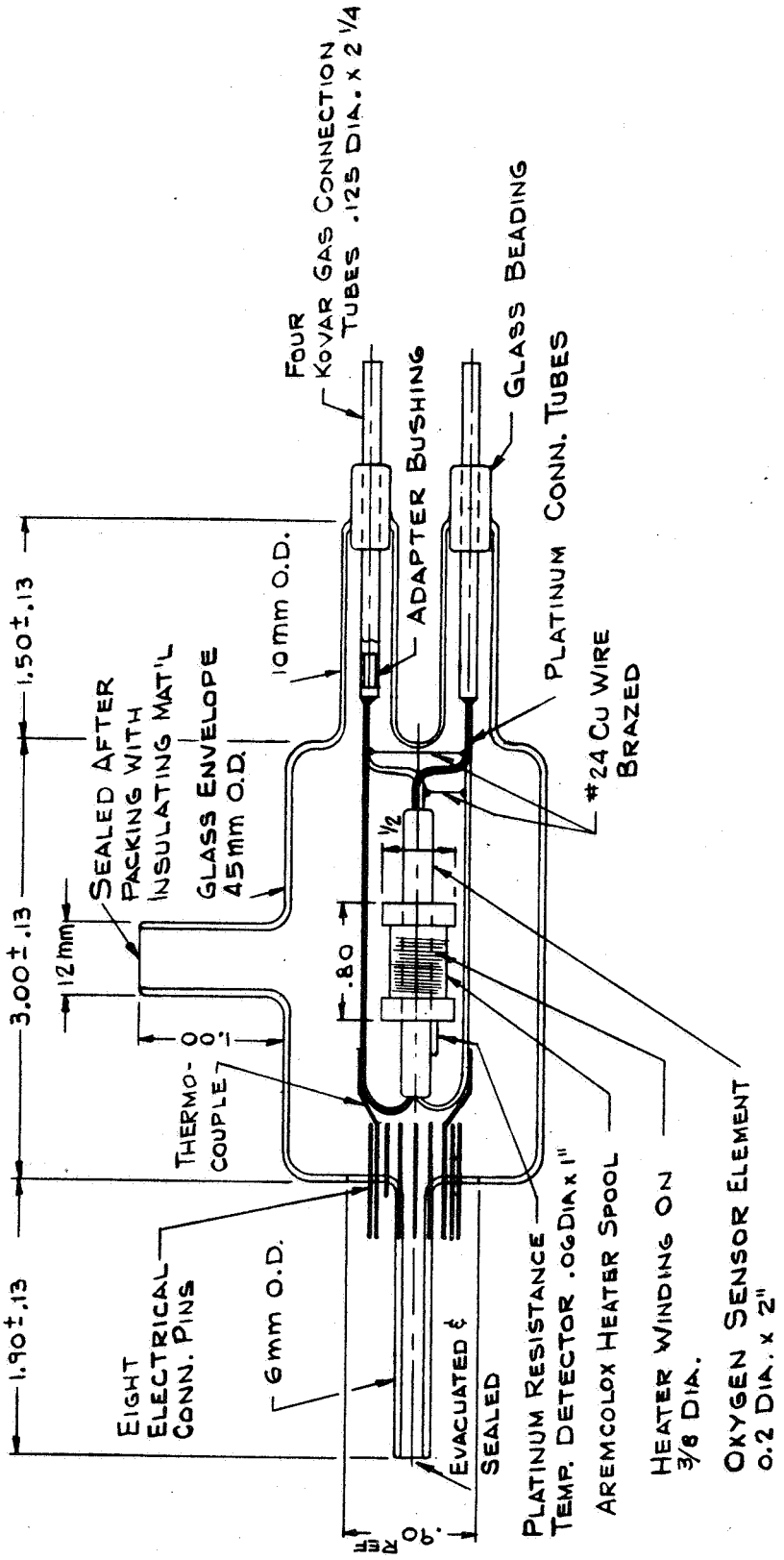


Fig. 15—Drawing of oxygen sensor

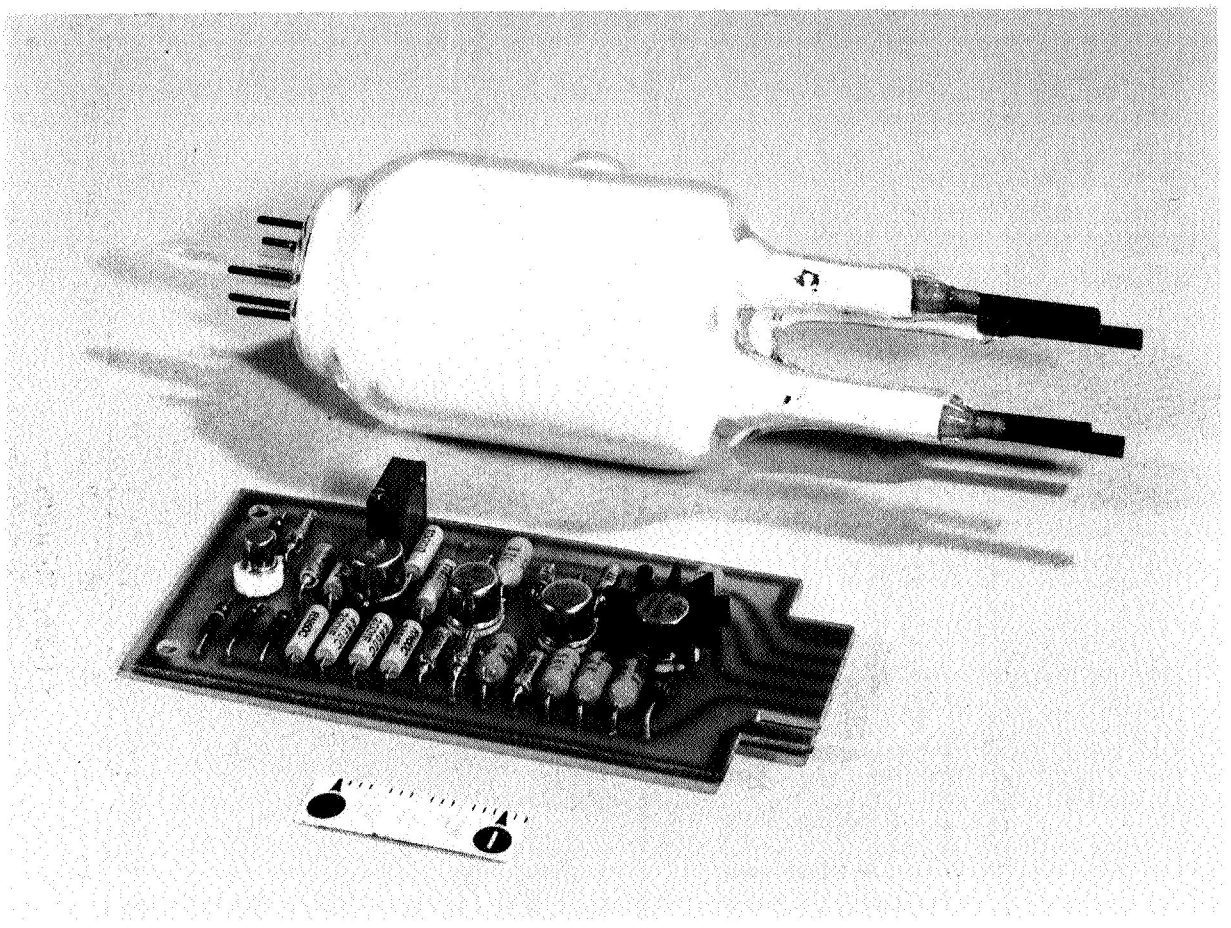


Fig. 16—Completed flight oxygen sensor and temperature controller

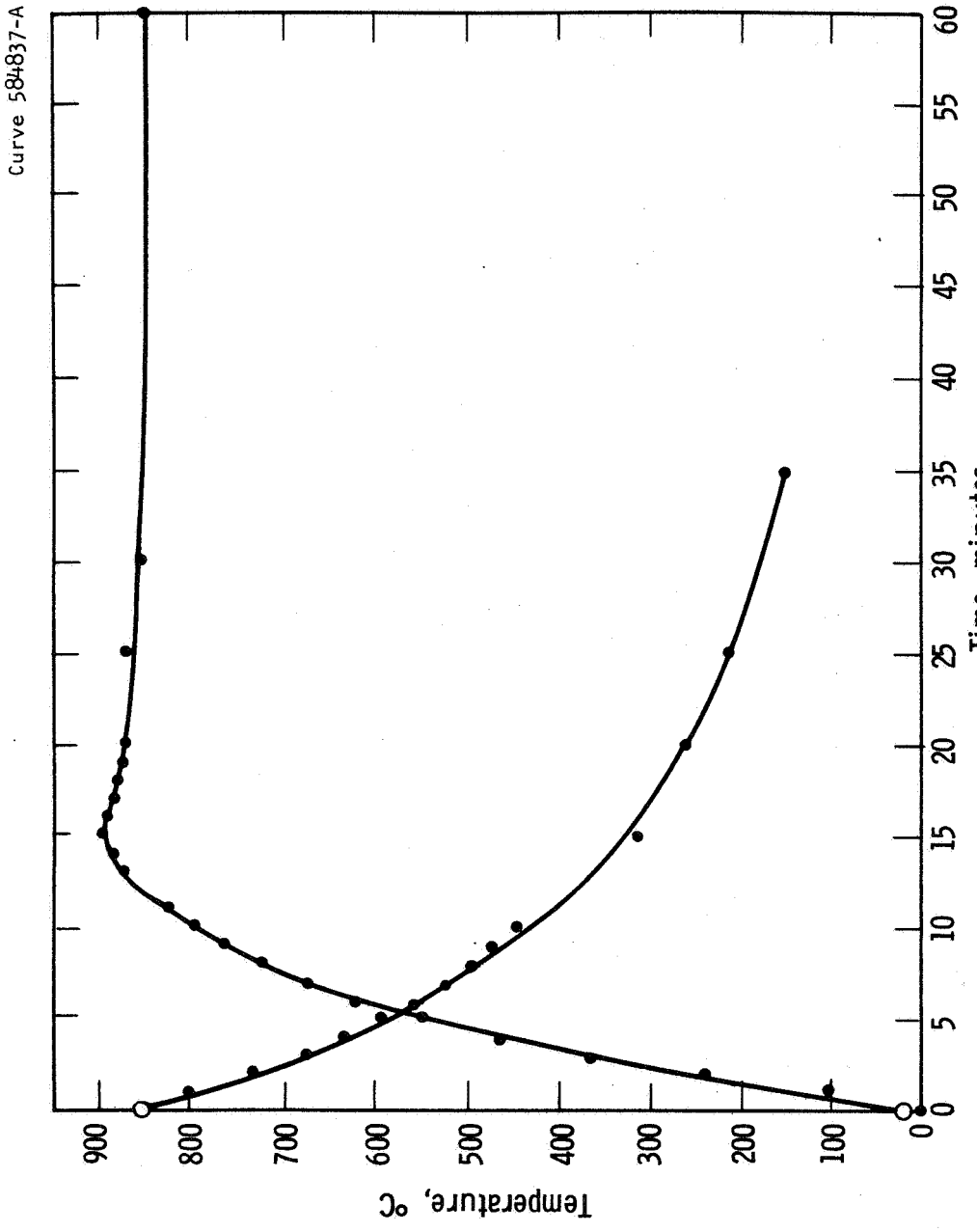


Fig. 17—Heating and cooling curves of sensor

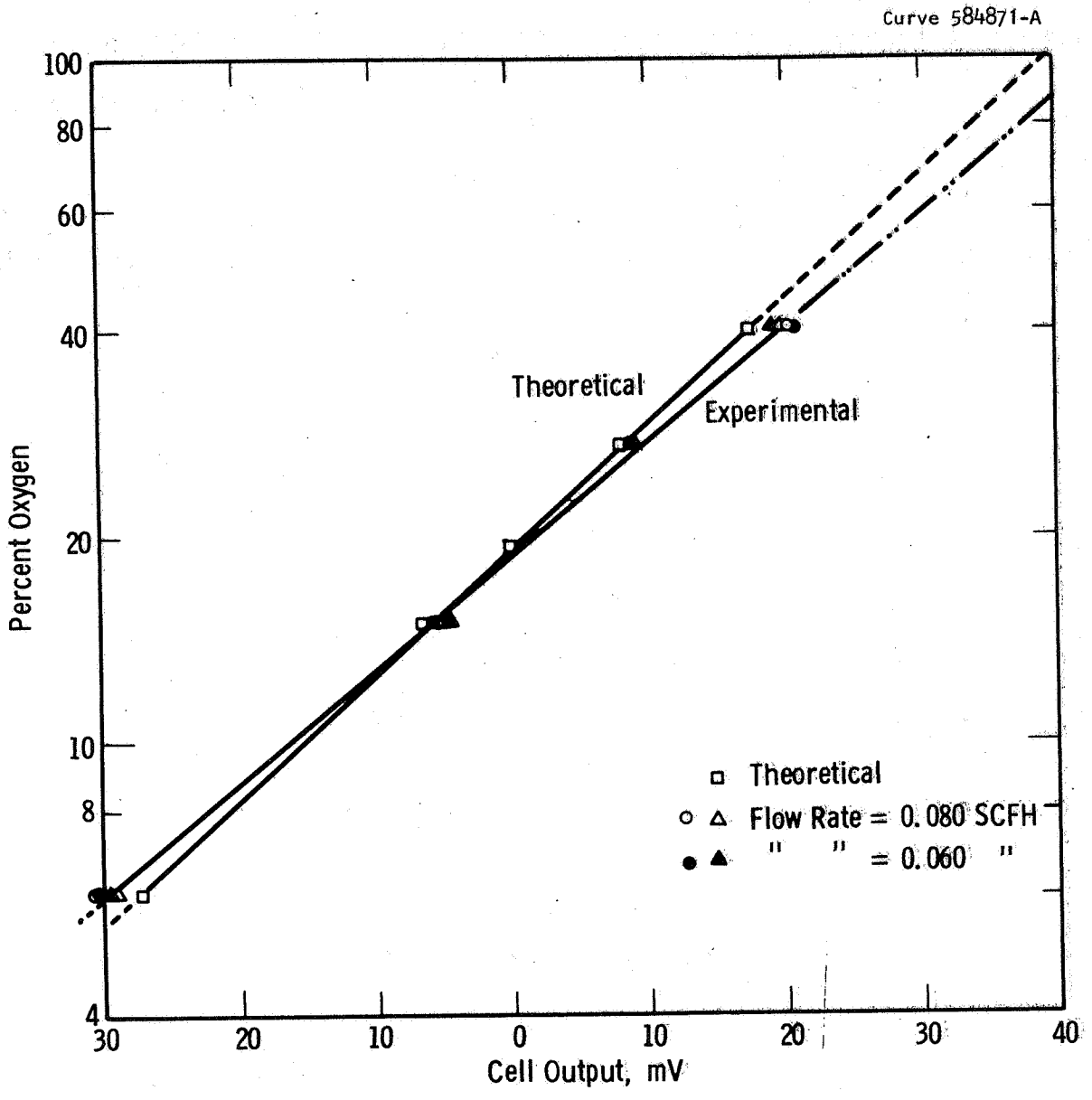
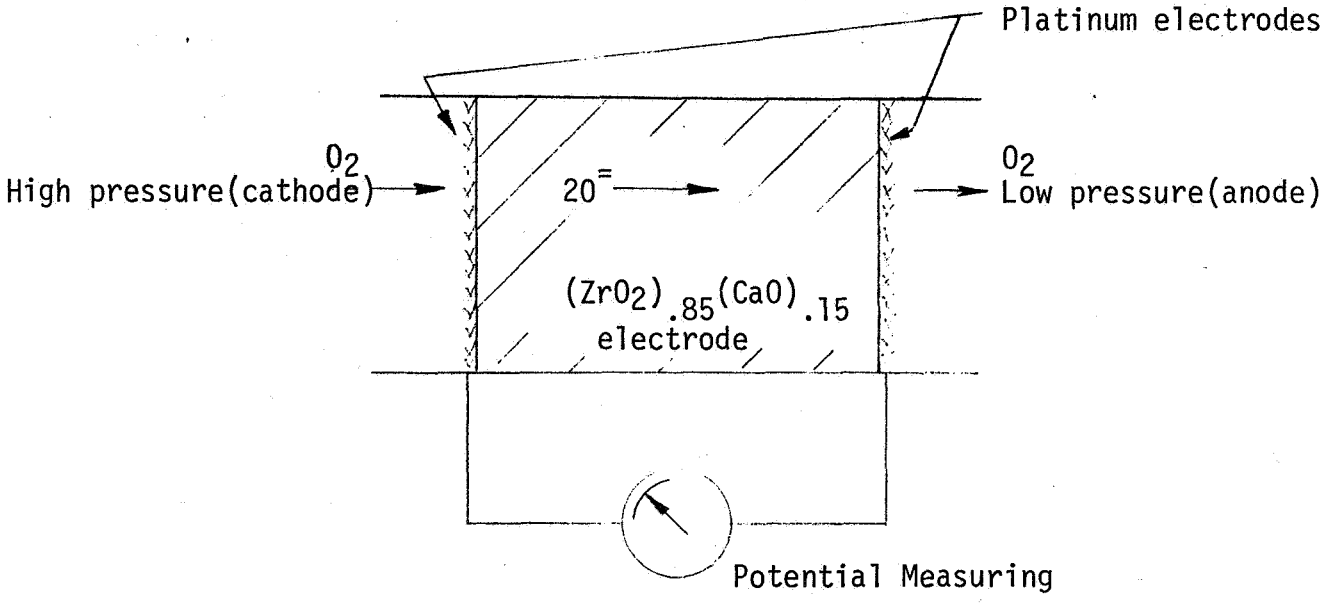


Fig. 18—Oxygen concentration versus cell output for flight sensor

APPENDIX

Theoretical Background Information

A simplified case of an oxygen concentration cell as used in the flight type oxygen partial pressure sensor is illustrated diagrammatically below:



Schematic of Oxygen Concentration Cell

In this cell the following reactions take place at the electrolyte-electrolyte interfaces:

$$\text{Cathode:} \quad O_2 + 4e \rightleftharpoons 2\ O^= \qquad (2)$$

$$\text{Anode:} \quad 2\ O^= \rightleftharpoons O_2 + 4e$$

At the cathode oxygen enters the electrolyte as oxygen ions. Simultaneously, at the anode, oxygen molecules are reformed by the reverse action.

The voltage E of this galvanic cell is related to the oxygen partial pressures at the electrodes by the standard Nernst relationship, for an oxygen concentration cell, equation 1.

For the sensors to be described in this report the equation for the open circuit signal voltage E, in millivolts, reduces to:

$$E = .0496\ T \log_{10} \frac{P_1\ (O_2)}{P_2\ (O_2)} \tag{3}$$

for those cells operating at 850°C the voltage E, in millivolts, is:

$$E = 55.7 \log_{10} \frac{P_1\ (O_2)}{P_2\ (O_2)} \tag{4}$$

In order for the cell to provide reproducible output voltages over extended periods of time, it is essential to prevent "poisoning" of the electrodes. This can be accomplished either by replacing the cell periodically as required or by operating at a temperature which will provide for the automatic removal of "poison" contaminants (850°C). The latter method has been adopted since it is most practical and also provides for a suitably low resistance to ionic conduction to eliminate the need for sensitive amplification of the output signal.

In order to operate at this high temperature, materials must be selected which have both suitable temperature stability, good ionic conduction properties and high electrical impedance. Such a material is zirconia doped with calcium oxide which provides stable crystallographic stability and suitable ionic conduction.

The conductivity in this material results from the presence of highly mobile vacancies at oxygen ion sites in the crystal lattice. One such vacancy exists for each Ca^{2+} ion in the lattice. The conductivity is due nearly

exclusively to oxygen ion or vacancy migration. Since electronic and metal ion conduction are virtually non-existent we have an ideal material for such applications.

If electronic conduction were present the cell EMF would be lowered while metal ion conduction would result in transfer of solid materials of the electrolyte and/or electrodes which would adversely alter the electrode-electrolyte interfaces.

The commercial Westinghouse oxygen analyzer measures the voltage generated by a galvanic cell to indicate the percent or ppm oxygen in an inert gas. This galvanic cell responds directly to the ratio of partial pressures of oxygen (and only oxygen) in contact with the two electrodes.

One electrode is in contact with the test gas, the other with ambient air. Since both gases are at atmospheric pressure and the same temperature, the ratio of partial oxygen pressure is the same as the ratio of oxygen concentration in the two gases.

The electrolyte separating the two electrodes is a special ceramic material which is a good insulator for electronic current flow but conducts oxygen ions when it is red hot. At 850°C the conductivity is so good (resistance so low) that a conventional millivoltmeter can be used to accurately measure the voltage produced by the cell.

The construction of the commercial cell is such that the test gas passes through the bore of a ceramic tube with ambient air freely circulating around the outside. Porous platinum electrodes are coated onto the inside and outside of the tube and connected electrically through the voltmeter.

Gas Laws

Daltion's Law of Partial Pressures $P_{total} = P_a + P_b + P_c + \ldots$

Boyle's Law $P_1V_1 = P_2V_2$

$P_1/P_2 = V_2/V_1$

Ideal Gas Law $PV = nRT$

When n = Number of moles (from here on n = 1)

R = Universal gas constant

T = Absolute temperature

so $p = RT/V$

Derivation of Thermodynamics of Analyzer

Work done by expansion of gas, constant temperature

$$W = \int_{V_1}^{V_2} p \, d \, V$$

For one mole

$p = RT/V$

$$W = RT \int_{V_1}^{V_2} dV/V = RT \ln \left(\frac{V_2}{V_1}\right)$$

$$\text{but} \quad \frac{P_1}{P_2} = \frac{V_2}{V_1}$$

$$\text{so} \quad W = RT \ln \left(\frac{P_1}{P_2}\right)$$

Also, for the maximum work-equivalent of a galvenic cell:

$W = n \, PE$

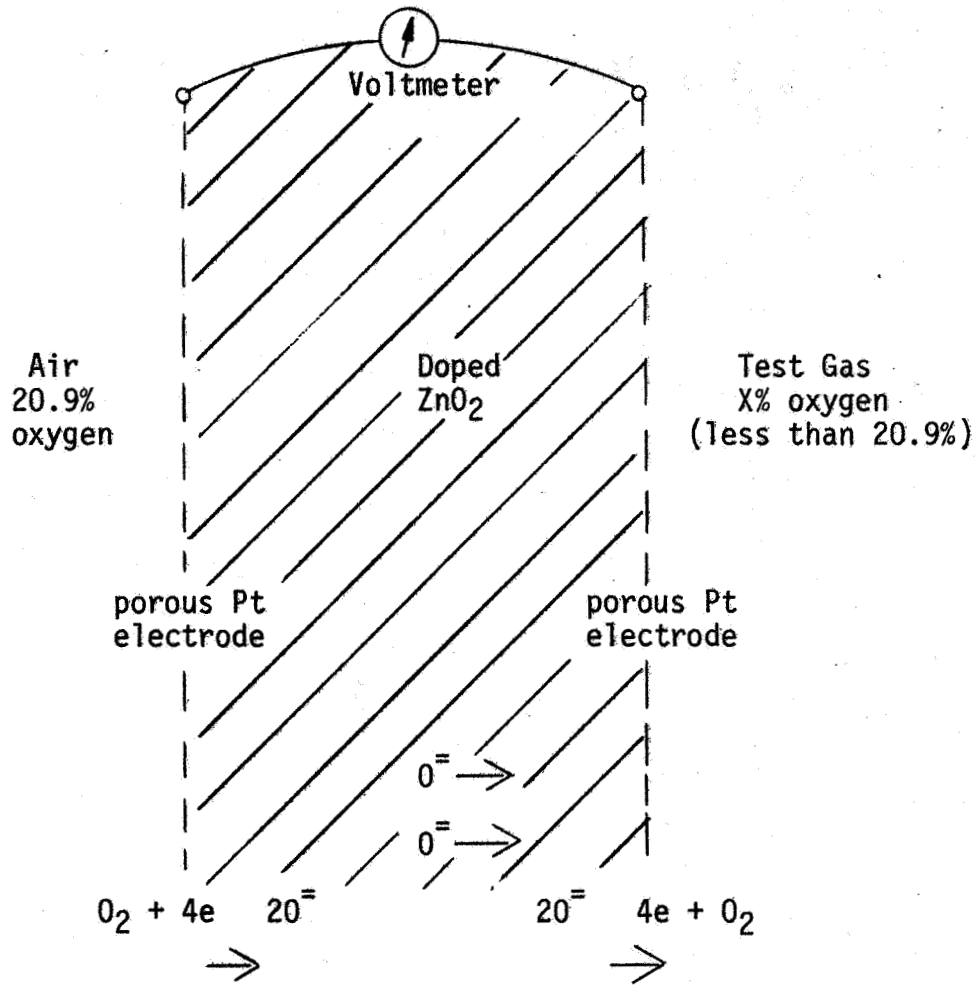
where n = number chemicals equivalent per mole of reaction

F = Faraday constant

E = EMF of cell

so $$E = \frac{RT}{nF} \ln \left(\frac{P_1}{P_2}\right)$$

For the cell:



at 850°C = 1123°K

R = 8.134

n = 4

F = 96,500

log 10 N = 2.303 ln N

then E = 0.0557 log (20.9/X)

where X = percent oxygen in unknown gas